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Report No. 8

on

Contract N6onr-22528 (NR039-005)

J. W. Spretnak and Rudolph Speiser

January 5, 1951

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Report No. 8

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By

The Ohio State University

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Cooperator:

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Washington 25, D. C.
Ordn Contract 1.6onr-22528 (1.RO39-005)

Investigation of:

Protection of Molybdenum Against
Corrosion at High Temperatures

Subject of Report:

Status during July 16 to December 31, 1953

Submitted by:

J. W. Spretak and Rudolph Speiser

Date:

January 5, 1954

Eighth Status Report on
ONR Contract N6onr-22528 (NR039-005)
For the period July 15 to December 31, 1953
The Ohio State University Research Foundation

Protection of Molybdenum Against Corrosion
at High Temperatures

I. INTRODUCTION

It has now been shown that molybdenum-nickel alloys, containing a sufficiently high percentage of nickel, form completely protective self-regenerative coatings on molybdenum in flowing air at 940°C. These coatings, which consist predominantly of nickel molybdate, spall violently off the alloy on cooling. A new coating is formed on reheating. Since repeated heating and cooling with resultant spalling must depreciate the nickel content of the alloy to the point where a protective coating can no longer be formed, work during the past months has been largely devoted to a study of the spalling of nickel molybdate.

A search is also being made for a compound which will prevent the spalling of nickel molybdate without spoiling its properties as a protective coating on molybdenum.

II. EXPERIMENTAL WORK

A. OXIDATION RESISTANCE OF MOLYBDENUM-NICKEL ALLOYS

Oxidation tests in flowing air at high temperatures were performed on the following alloys: 95% Mo-2% Ni; 85% Mo-15% Ni; 80% Mo-20% Ni; 70% Mo-30% Ni; 62% Mo-38% Ni and 70% Mo-10% Ni-20% Cr.

These specific alloys were chosen because there was already some indication that increasing the percentage of nickel in molybdenum alloys will

produce more effective protective coatings. The 62% Mo-38% Ni alloy corresponds to equiatomic proportions of molybdenum and nickel. It should also correspond to the formation of a single phase, known as the δ phase, in the molybdenum-nickel diagram¹. The 70% Mo-10% Ni-20% Cr alloy was reported by Battelle Memorial Institute² to be oxidation resistant at high temperatures. It was thought also, for reasons which are explained later in this report, that there was some possibility that the coating on the latter alloy at high temperatures would not spall.

Apparatus and procedure for these tests were described by J. F. Mosher^{3,4} in previous reports. The technique permits weighing of the oxidizing specimen at any time during the test.

An approximately orthorhombic sample of the alloy 98% Mo-2% Ni with surface area of 10.3 cm² and a minimum thickness of 0.8 cm. became completely oxidized to nickel molybdate and molybdenum trioxide powder after heating for nineteen hours at 942°C. A graph of weight loss/unit area vs. time has not been plotted for this specimen as it lost weight so rapidly, with resultant unknown changes in area, that a computation of the weight loss in g/cm² was not possible.

Results of tests on the other alloys are recorded in Figures 1 and 2. It has not been considered justifiable to draw in a smooth curve in all cases. The interpretation of the shape of these graphs was given in the previous report.

The following observations were made:

1. As the percentage of nickel in the alloy increased the protectivity of the coating increased.
2. The 70% Mo-30% Ni and the 62% Mo-38% Ni alloy formed completely

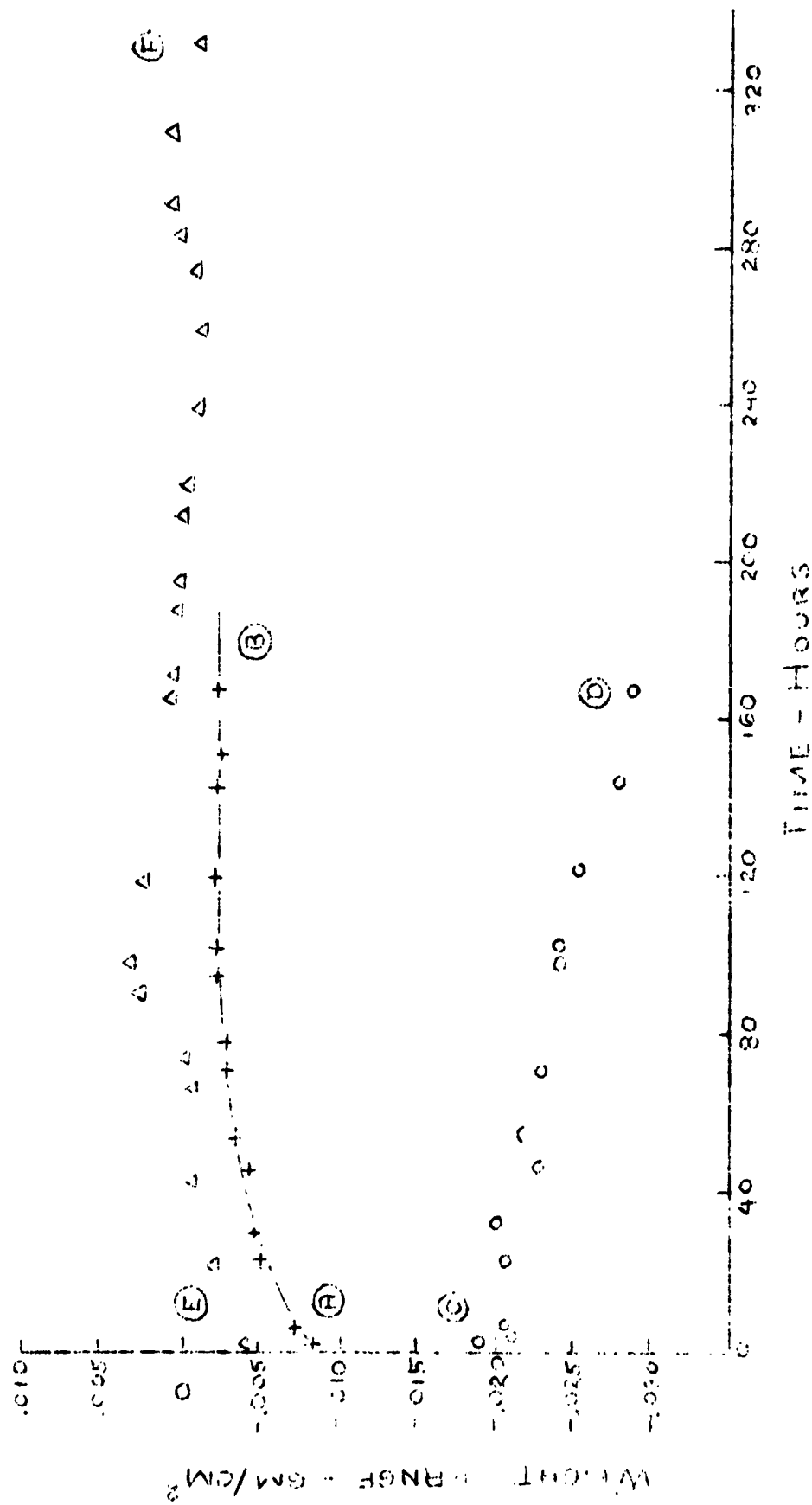


FIGURE 1 OXIDATION CURVES FOR MOLYBDENUM - NICKEL ALLOYS

	58% NICKEL	930°C
+	30% NICKEL	940°C
o	20% NICKEL	940°C

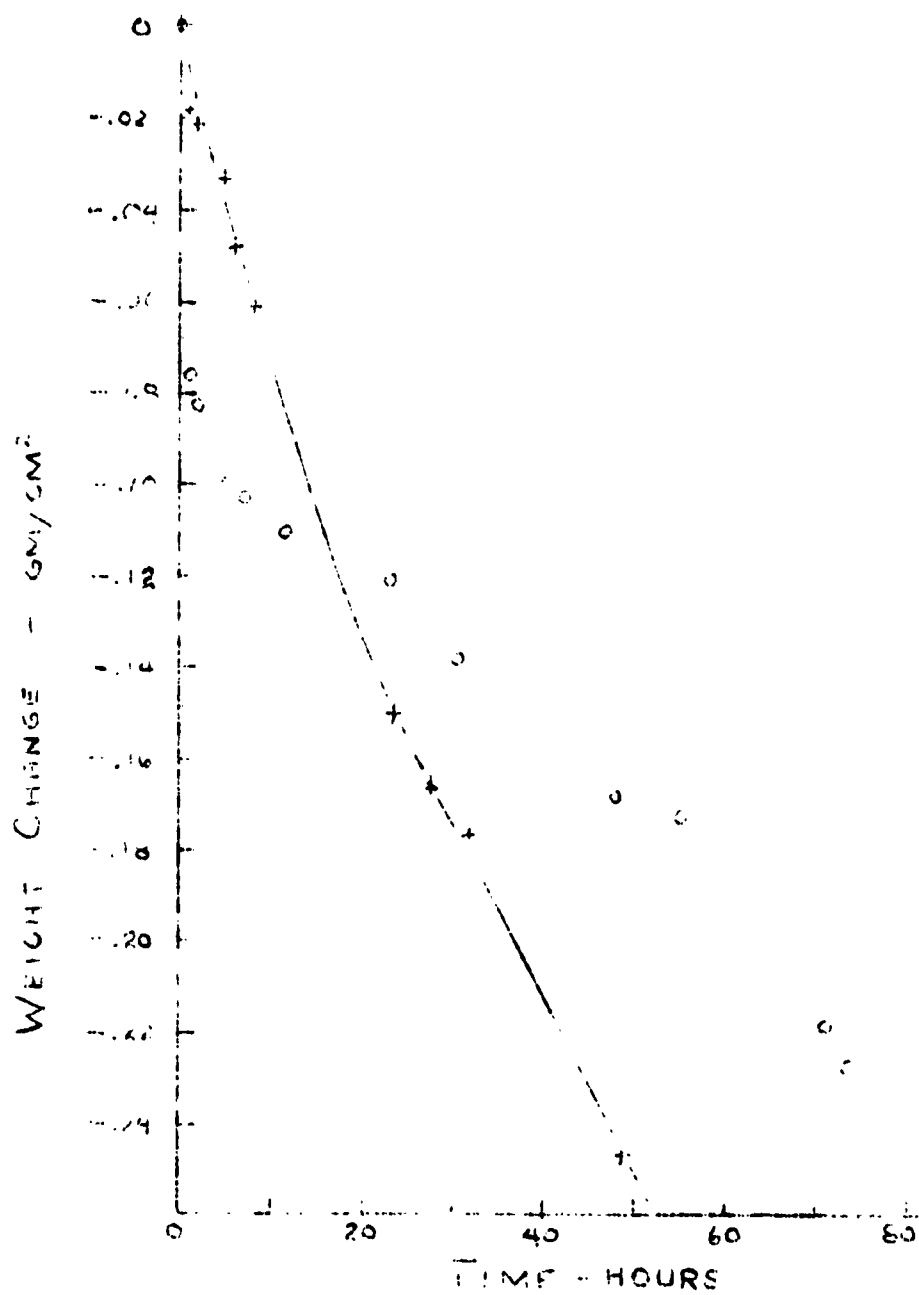


FIGURE 2

OXIDATION CURVES - MOLYBDENUM BASE ALLOYS

O 15% NICKEL 950°C

+ 10% NICKEL - 20% CHROMIUM 940°C

protective coatings.

3. The coating on the 70% Mo-30% Ni sample on removal from the furnace changed from a light yellow-green to a dark green color as it spalled in the manner characteristic of nickel molybdate. It was identified from its X-ray diffraction pattern as being predominantly nickel molybdate. On replacing the same sample in the furnace a second curve of the same form as AB (Figure 1) was obtained indicating a second protective coating had formed. It may be deduced that nickel molybdate forms a completely protective coating on molybdenum. In the molybdenum-nickel alloys in which the nickel content is low the nickel molybdate formed is insufficient to cover the surface of the alloy completely and is therefore not completely protective.

4. The 70% Mo-10% Ni-20% Cr alloy gave only a partially protective coating. On removing this alloy from the furnace, the coating spalled. It was identified by its X-ray diffraction pattern as being predominantly nickel molybdate (NiMoO_4) and chromic oxide (Cr_2O_3). Since the coating on a 70% Mo-30% Ni alloy is completely protective, it is apparent that chromic oxide plus nickel molybdate is less protective than nickel molybdate alone.

5. The oxidation test performed on the 80% Mo-20% Ni (CD, Figure 1) alloy for a prolonged period shows that this alloy forms only a partially and not a completely protective coating as was previously thought. The fact that the points do not lie on a smooth curve may be due to the kinetics of formation of the coating.

6. The points on the curve EF for the 62% Mo-38% Ni alloy are also somewhat scattered. The significance of the scatter is unknown.

B. SPALLING OF NICKEL MOLYBDATE

(a) General Theory of Spalling

The phenomenon of spalling may be produced as a result of one or more independent causes⁵.

In a homogeneous material like nickel molybdate, spalling, which is observed as a fragmentation of part of the sample, could be due to one or both of two causes. It could result from an atomic disregistry occurring when all or part of the sample undergoes a phase change. This will be referred to in this report as structural spalling*, being of the type in which a change in crystalline structure is involved. It is commonly found in quartz on heating or cooling through the α - β inversion between 500° and 600°C. In quartz, this phase change is associated with a volume expansion as great as 1% which, added to the effect of the structural change, further contributes to spalling⁷. Spalling could also occur without a phase change being present provided that there were a temperature gradient across the sample, that the coefficient of expansion were sufficiently great and that the thermal conductivity and elasticity were small. This type of spalling will be referred to as non-structural spalling to indicate that a change in crystalline structure is not involved.

In order to resist spalling a substance should possess great elasticity and high ultimate shearing strength so that it will withstand thermal shock. Thus metals, with their high elasticity, rarely spall. A substance should also have a low coefficient of expansion and a high thermal diffusivity in

*It should be noted that in the technical literature⁶ the expression "structural spalling" is not used as above. It is used elsewhere to cover the type of action occurring in refractories which partially undergo a marked irreversible change in their structural or physical properties after prolonged exposure to high temperatures and slags or fluxes.

order that great stresses will not be produced^{7,8,9,10,11}.

In the case of spalling of a layer of nickel molybdate from an alloy, the phenomenon may also be due to a high differential coefficient of expansion between the alloy and nickel molybdate, causing the nickel molybdate to fall away.

In order to suppress spalling it is necessary to understand which type of spalling is occurring. A number of experiments have been carried out with this end in view.

(b) Mechanism of Spalling in Nickel Molybdate

First it must be noted that spalling of a nickel molybdate coating from a molybdenum core is not due solely, if at all, to a high differential coefficient of expansion between the two, since nickel molybdate alone spalls to a considerable degree.

Very slow cooling of specimens should eliminate spalling of the non-structural type since this type of spalling depends upon a temperature gradient existing. Elimination of spalling by slow cooling, therefore, would prove that it is of a non-structural type, since structural spalling depends only on a change of phase which should occur regardless of how slowly the material is cooled. Failure to eliminate spalling in this manner would not be definitive since it may simply be that the rate of cooling was insufficiently slow. A specimen of nickel molybdate and a piece of 70% Mo-30% Ni alloy were therefore placed in a uniform temperature zone in an oven and heated to 928°C. The oven was cooled very slowly, the rate being given in Figure 3. On reaching room temperature, both specimens were found to have spalled. This experiment, therefore, turned out to be of an inconclusive nature. It is interesting to observe, however, that the rate of cooling was very slow indeed

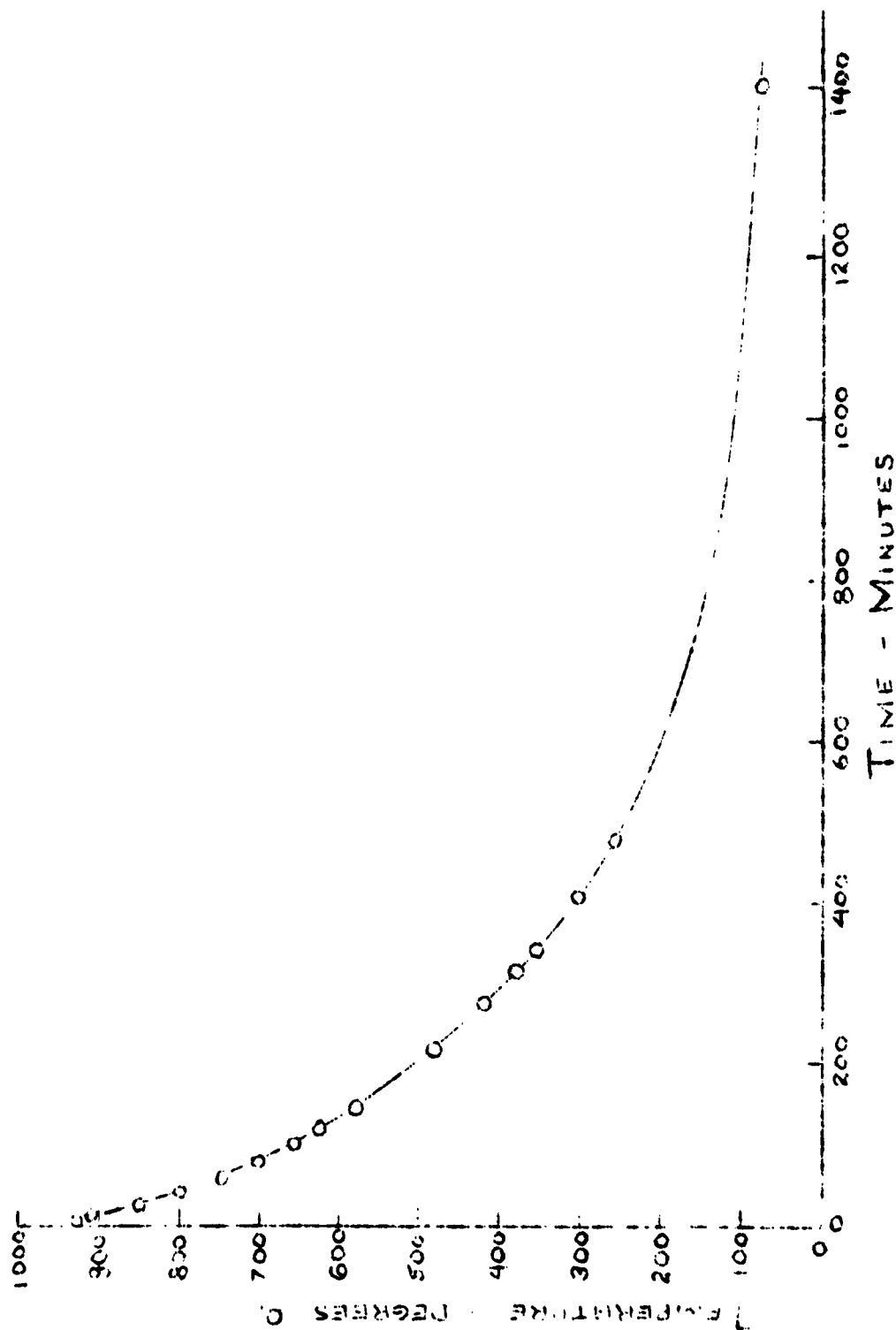


FIGURE 3. COOLING CURVE FOR NICKEL MOLYBDATE

so that the experiment is indicative, but not proof, of the existence of structural spalling.

An experiment was carried out to find if the temperature of spalling corresponded to a phase change in nickel molybdate. It was noted that spalling occurs both on heating and on cooling although more violently on cooling. Spalling during heating occurs between 240° and 400°C. On cooling from 975°C, spalling occurs between 226° and 110°C. Referring to the differential thermal analysis data obtained, it does not appear that spalling occurring on heating could correspond to a phase change; however, there is some possibility that spalling on cooling does correspond to low temperature transitions recorded on the nickel molybdate thermogram. What appear to be low temperature transitions in the thermograms may actually be differential temperatures due not to crystalline changes but to spalling and subsequent changes of environment surrounding the thermocouple tips. The fact that they do not correspond in number, temperature or heat change to the transformations obtained on heating indicates some likelihood of this. This experiment again points to the probability of non-structural spalling.

Some nickel molybdate in a platinum crucible was heated over a Meker burner for a few minutes and then quenched in ice water. Some of the nickel molybdate spalled violently onto the sides of the crucible. The spalled powder was identified from its X-ray diffraction pattern as being predominantly the high temperature form of nickel molybdate. This again seems to indicate non-structural spalling. This experiment also is not conclusive since there were minor lines in the X-ray diffraction pattern which were unaccounted for. It was possible also that the powder thrown onto the sides of the crucible had not itself spalled but was thrown up by a small amount of powder spalling

inside the mass of the nickel molybdate. This experiment will be repeated and an examination made both of spalled powder on the sides of the crucible and of the residue.

(c) Elimination of Spalling

It was thought that since spalling is less likely to occur in elastic substances, addition of substances with higher elasticities, such as alumina or chromic oxide, to nickel molybdate, might prevent its spalling. Unfortunately, spalling was not prevented. Mixtures of alumina and nickel molybdate and of chromic oxide and nickel molybdate were heated to 1200°C. On cooling, the mixtures spalled in the usual manner; no reaction between the components appeared to have occurred. In agreement with these experiments is the fact that the coating of nickel molybdate and chromic oxide formed on a 70% Mo-10% Ni-20% Cr alloy during oxidation spalled violently on cooling from a high temperature.

An intimate mixture of magnesium molybdate and nickel molybdate in approximately equimolecular proportions showed only very little spalling, at least by visual examination, on cooling from 1200°C. An X-ray diffraction pattern of the cooled sample showed it to consist of the high temperature forms of magnesium and nickel molybdates. No reaction had apparently occurred between the two at 1200°C. The mechanism by which the spalling was reduced is not yet understood.

C. X-RAY DATA

An interesting phenomenon has been noted in the X-ray diffraction patterns of magnesium molybdate.

The differential thermal analysis of anhydrous magnesium molybdate**

**Erratum. The X-ray data given for magnesium molybdate in Report #5, pages 10-13, Contract N6onr-22528 (NR034-404), January 15, 1953 are not those of anhydrous magnesium molybdate as was previously supposed, but of one of the hydrated forms.

showed one small exothermic transition believed to indicate a phase change at 827°C on heating. The high temperature form is retained on cooling to room temperature³. Magnesium molybdate should, therefore, exist in two crystalline forms, one stable up to 827°C and the other stable above this temperature. It was expected that it would be possible to obtain X-ray photograms of the pure phases for the two forms by quenching from within the appropriate temperature range. Single-phase patterns were not observed, however. Samples quenched after heating for 45 minutes at 575°C and 20 hours at 656°C, which should produce only the low temperature phase, produced photograms containing the principal lines occurring in a sample quenched from 1208°C, which should be the high temperature phase. A sample quenched after heating for 2-1/4 hours between 852° and 879°C showed very clearly the principal lines of the low temperature phase in addition to the lines of a high temperature phase.

The above results could be caused by either:

(1) Some kind of slow chemical reaction occurring in magnesium molybdate or (2) an extremely sluggish phase change which occurs very slowly at 575°C and becomes rapid only at about 827°C. It seems rather unusual that a phase change should occur so slowly at temperatures this high.

It has already been shown that magnesium molybdate heated to 1080°C and subsequently cooled to room temperature is stable and insoluble¹³ but further experiments over prolonged periods will be carried out to recheck this point. If cause (1) is eliminated by these experiments then (2) will be investigated more fully.

It is of interest to remember that similar results were obtained with nickel molybdate. Nickel molybdate samples quenched from as much as 40°C below the transition points show evidence of the appearance of the principal

lines of the high temperature form. Investigation of this peculiarity is easier in magnesium molybdate when spalling does not add a further complication. It is possible that by analogy illumination also will be thrown on the phenomenon as it occurs in nickel molybdate.

Owing to the confusion existing in the presence of lines characteristic of the high temperature phase in what should be the low temperature phase, and to the lack of understanding of this problem, the X-ray data for the two forms of magnesium molybdate and the phases of nickel molybdate will not be tabulated in this report.

III. CONCLUSIONS AND FUTURE WORK

Molybdenum-nickel alloys, in which the percentage of nickel is sufficiently high, have now been shown to be definitely capable of forming completely protective coatings at high temperatures. These coatings spall destructively on cooling. It must be emphasized that evidence collected in this and the previous report on the spalling of nickel molybdate is contradictory, as yet, and that experiments now planned or in progress must be completed before definite conclusions can be drawn.

One of the difficulties in investigating the spalling phenomenon is that the differential thermal analysis of nickel molybdate³ showed complicated behavior which is not yet properly understood. It is possible that even non-structural spalling is accompanied by real or apparent heat changes which were recorded on the thermograms. It is possible also that the nickel molybdate contained small amounts of contaminants which may effect X-ray patterns and thermograms. Such an explanation might account for "extra" lines appearing in the high temperature forms of nickel molybdate after quenching from various temperatures above the transition point¹².

In the immediate future, work will be directed primarily as follows:

(1) Nickel molybdate will be prepared by different methods in order to improve upon the purity of the compound previously used.

(2) Differential thermal analysis of pure nickel molybdate will be carried out. X-ray diffraction patterns of nickel molybdate will be obtained at the conclusion of these experiments in order to see if the lower thermal transitions occurring on cooling correspond to re-formation of the low temperature form of nickel molybdate, or whether they correspond to non-structural spalling.

(3) Further tests will be performed on suppression of spalling on nickel molybdate by addition of certain oxides or molybdates.

(4) Preparation of a single crystal of nickel molybdate will be undertaken by recrystallization from aqueous solution as there is some evidence that nickel molybdate is very slightly soluble in water. If this method fails, an attempt will be made to grow a single crystal by slow-cooling of liquid nickel molybdate through its melting point provided melting takes place without decomposition. The melting point of nickel molybdate is not yet known but it is above 1200°C. If a single crystal of nickel molybdate is prepared, an attempt will be made to determine the structure of nickel molybdate by X-ray analysis.

(5) Spalling of cobalt molybdate, which is isomorphous with nickel molybdate, will also be investigated since it may throw some illumination on the phenomenon as occurring in nickel molybdate.

(6) An attempt will be made to resolve the confusion existing in the X-ray data obtained for the different phases of magnesium and nickel molybdates.

ACKNOWLEDGEMENTS

We thank the Battelle Memorial Institute for their ready cooperation in preparing and supplying the molybdenum alloys used in this investigation.

NOTE: In submitting this report it is understood that all provisions of the contract between the Foundation and the Cooperator and pertaining to publicity of subject matter will be rigidly observed.

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